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(56) Documents cited
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(54) An anti-stokes luminescent material

(57) The material disclosed comprises doped yttrium oxysulphide (Y_2O_2S), in which the dopants comprise, by weight of the oxysulphide, 4 to 50% of one or both of erbium (Er) and ytterbium (Yb). The material may comprise 1 to 50 ppm of one or more other lanthanide elements. Erbium and ytterbium may be replaced by thullium (Tm), holmium (Ho) or lutecium (Lu).

The material may be in the form of particles whose average size is no more than 20 μm.

The material may be used in inks for printing e.g. security documents because they are invisible under normal viewing conditions and visible when illuminated with infrared illumination.

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LUMINESCENT MATERIALS AND THEIR USE IN SECURITY DOCUMENTS

This invention relates to security documents and to materials that can be used as markers, for use in authenticating such documents and thus preventing counterfeiting.

Luminescent materials such as fluorescent and phosphorescent materials are commonly used in banknotes and the like for security verification purposes. The commercially-used luminophors obey Stokes Law, in that their emissions are at a lower energy than that of the exciting radiation. For example, such materials when illuminated with ultraviolet radiation will emit in the visible.

Anti-Stokes or, as they are otherwise known, "upconverting" materials emit light (visible or ultraviolet) which has a shorter wavelength than the activating radiation. For the purposes of this specification, anti-Stokes materials absorb infrared radiation, typically from 700 to 1300 nm, and emit in the visible. Anti-Stokes materials emit photons at higher energy, and this can occur if two or more incident photons result in one emitted photon (of higher energy). Anti-Stokes materials have seen limited application to security items.

Inorganic luminescent pigments are normally refractory solids and, if the particle size is reduced by grinding, then their luminescent efficiency decreases rapidly, as is well known. Unfortunately, the smallest acceptable anti-Stokes material particle size previously available is much larger than is normally acceptable for security printing inks. It has not hitherto been possible to make satisfactory ink formulations which contain anti-Stokes materials suitable for the main security printing methods, i.e. intaglio, letterpress or lithography, owing to their requirement for small particles.

For use in currency, particularly severe demands are placed on inks. The inks must retain their properties for

the life of the document, withstanding the rigours and challenges of handling, wetting and contamination. Similarly stringent properties must also apply to other security documents which have a long life and whose value is associated with the integrity of the document.

Security documents by their very nature need to incorporate a variety of different measures in order to defeat counterfeiting. At one extreme, visual measures are designed to be seen with the naked eye. At the other extreme, sophisticated and expensive detectors may be employed, say attached to banknote sorting equipment, to validate banknotes and the like. ~~Many of these features~~ may be invisible under normal viewing conditions.

US-A-4047033 discloses documents including anti-Stokes fluoride materials. Such materials are generally unsuitable for security documents, however, since they are liable to hydrolysis which causes a reduction of their luminescence, and because they are difficult to produce in finely particulate form, i.e. less than 20 μm in size. The particles disclosed in US-A-4047033 are adapted for screen inks, and are therefore relatively large.

GB-A-2089385 discloses ferrite, perovskite and garnet-type storage phosphor materials for security documents that absorb in the IR, emitting in the UV.

AU-A-0562509 and AU-A-0571276 describe fluoride, oxide or mixed rare earth oxyfluoride anti-Stokes luminescent materials and their use in security documents. Inks are not described. Some of such materials are liable to hydrolysis; they are difficult to reduce to a suitably small particle size while maintaining fluorescence efficiency. The former document discloses precipitation, sieving and crushing, to obtain small particles.

US-A-4387112 discloses credit cards marked with inorganic storage phosphors, e.g. a mixed phosphor such as SrS(Eu,Sm). They are used in finely-divided form, apparently after grinding. The luminescent properties of almost all phosphors are adversely affected by grinding.

According to the present invention, an anti-Stokes luminescent material comprises doped yttrium oxysulphide, in which the dopants comprise, by weight of the material, 4 to 50% total weight of Er and/or Yb, and 1 to 50 ppm of one or more other lanthanide elements.

A material of the invention can be provided in the form of particles which are suitable for use in printing by intaglio, letterpress or offset lithography. For this purpose, the particles have a maximum diameter of no more than 40 μm, more preferably no more than 20 μm, and most preferably below 10 μm, e.g. 1 to 5 um or even 1 to 2 μm. Particles of such a size can be produced, without grinding, by the process described in another patent application filed in the name of Thomas De La Rue and Company Ltd and on the same day, entitled "Luminescent Materials and Their Preparation", in which oxides of the rare earths are fused with sulphides or elemental sulphur, the fused mass is leached with water to extract soluble residues. Some milling may then be appropriate, depending on the desired particle size.

The oxysulphide has the general chemical composition Y_2O_2S:A, where A is a primary rare earth dopant selected from Yb and Er, or a mixture of Yb and Er. One such composition, i.e. Y_2O_2S:Yb,Er, is usually characterised by green emission on IR stimulation.

The total level of doping is generally no more than 30%, and typically less than 25%. For example, the material comprises 2 to 10% Er and 5 to 15% Yb. The weight ratio of Yb to Er may be about 1:3.

Other rare earth elements can have a marked effect on luminescent properties, even when present in very small amounts. The amounts of these elements present must be carefully controlled. In the case of Y_2O_2S:Yb,Er, good results may be achieved if one or more of La, Ce, Pr, Nd, Sm, Eu, Cd, Tb and Dy is present in an amount of less than 3 ppm and, in certain instances, less than 1 ppm. Higher

levels of Ho, Tm and Lu can improve luminescent efficiency, when present at 2-20 ppm.

The purity of the starting materials will determine the performance of the product. It is preferred to use at least 99.999% pure yttrium oxide, and at least 99.99% pure ytterbium and erbium oxides.

The doped oxysulphide may be prepared by firing a blend of, say, BDH Chemicals Ltd "AnalaR" quality flux materials with pure yttrium oxide, ytterbium oxide and erbium oxide, e.g. at 1100°C for 1 hour. The firing time and temperature may be varied within the ranges 0.5 to 4 hours and 1000 to 1200°C, while 1050-1150°C and 1-2 hours give consistent results. A firing schedule of 1 hour at 1100°C is suitable.

The ratio of ytrrium : ytterbium : erbium in the blend, before firing, may be varied. Some increase in brightness may be obtained by adjusting the ytterbium content.

The value of the materials used in the present invention includes their stability and their high anti-Stokes efficiency. They are therefore useful as markers in security documents, for preventing counterfeiting.

Security items are items whose value is established or increased by being difficult to counterfeit or alter fraudulently. Examples of security documents, which may incorporate materials of the invention, are banknotes, currency, share certificates, bonds, passports, driving licences, permits, travel tickets, lottery tickets, plastic credit cards, charge cards, cash withdrawal cards, cheque cards, travellers' cheques and bank cheques, smart cards and remote access control cards.

A security document incorporating a material of the invention may conveniently be prepared by applying an ink containing the material. The security printed item may be a banknote.

The ink will normally be used to print, by letter press, intaglio or offset, invisible designs and security

features. Alternatively, the materials may be incorporated into coloured inks, to enhance the anti-counterfeiting level of the printing. This may be, for example, by incorporating the material into a banknote-numbering ink.

Intaglio inks and letterpress are preferred. Letterpress can achieve 5 μm of ink film. Intaglio ink printing can give printed thicknesses of, say, 5 to 70 μm.

An ink of the invention comprises, in addition to the anti-Stokes material, conventional components such as a colourant and a vehicle. For example, the ink may be prepared by thoroughly mixing an extender, wax, anti-Stokes material and any other security additives with resins components of an ink vehicle, and a hydrocarbon solvent. These components are then further dispersed, typically using a triple-roll mill, at a suitable pressure. Once the correct degree of dispersion has been reached, further solvent and other components are added.

A security document of the invention may be authenticated by irradiation with infrared light, and observation of the visible light thus produced. The means of irradiation may be, for example, a near infrared-emitting gas laser, laser diode or infrared-emitting diode. Laser diodes or infrared emitting diodes, for example GaAs(Si) emitting at 940 nm, may conveniently be employed with matching materials. Alternatively, tungsten-halogen light sources, suitably filtered to remove visible light, may be used.

The materials of the invention have relatively narrow absorption and emission bands. The emission of the illuminating source must therefore be matched to the absorption of the material and, in the case of machine-reading, this must be matched to the detector. Photodetectors tend to have wide absorption bands which may be narrowed by the use of filters or spectral discriminators.

For the purposes of this specification, the ultraviolet, visible and infrared regions cover from 200 to

399 nm, 400 to 699 nm, and 700 to 1300 nm, respectively. The printed ink may be viewed by exposure with an infrared diode emitting at approximately 940 nm (peak wavelength).

Materials of the invention normally will exhibit a shift of at least 100 nm from the illuminating source, and preferably of 200 nm or more. For example, on irradiation with an infrared diode emitting at a peak wavelength around 940 nm, it is possible to observe orange, green, yellow-orange fluorescences.

An advantage of the invention is that it is not obvious from visible examination of the, say, intaglio printing that the printing has an infrared responsive emitter. The effect is not obvious in its own right, and there are of course many possible physical effects which might be used. Such an effect is therefore deeply hidden, and it will therefore not be readily detectable by a potential counterfeiter.

In order to disguise the effect of those materials which do not themselves luminesce on exposure to ultraviolet illumination, it is possible to mix normal (Stokes) luminophors with the material. In certain cases an IR-activated upconverting luminophor which emits in the visible may cause a fluorescent material of matching absorbance to emit at a longer wavelength.

Compositions according to the invention may be prepared by a standard procedure in which the lanthanide element is already present in the particular type of yttrium oxide used. Control materials, lacking the lanthanide level necessary for the purposes of the invention, may also be prepared by the same method, but using yttrium oxide which has a low lanthanide level.

The possibility of replacing Yb and/or Er with one or more of HO, Tm and Lu is also envisaged.

The following Examples 1 to 5 illustrate materials of the invention (the procedures described immediately above are adopted, as appropriate). A variety of materials, including a reference, is analysed in Examples 2 to 6.

Examples 7 to 15 describe formulations which may be made with any of the luminescing products of the invention. "3N's Grade" and "4N's Grade" indicate a purity of respectively 99.9% and 99.99%.

The starting components should be of the highest purity available as is usual in the preparation of phosphors.

Example 1

The following materials were milled together in a pint size porcelain mill jar with porcelain balls for 2 hours:

78.74 g	yttrium oxide (3N's grade)
14.96 g	ytterbium oxide (4N's grade)
6.30 g	erbium oxide (4N's grade)
250 ml	water

After milling, the porcelain balls were separated from the slurry of rate earth oxides, the latter was filtered and the mixed rare earth oxides were dried and then sieved.

20 g of this mixed oxide powder was intimately mixed with:

7.48 g	potassium fluoride
5.52 g	sodium carbonate
5.52 g	sulphur

and heated at 1100°C for 1 hour in a covered alumina crucible. When cool, the fused mass was soaked in water until it softened down to a fine powder which was then filtered off, washed with more water, dried and sieved. This material, on irradiation with IR emitted green radiation. The material was then milled.

The particle size was determined microscopically and at least 90% of the particles had a maximum diameter of less than 40 μm.

In addition to using the purest available components, the crucible was of recystallised alumina. Contamination was avoided wherever possible.

Ytrrium oxysulphide phosphors are usually fairly resistant to grinding, but can be prepared in fine particle

size ranges. Milling can be used to reduce the particle size further but generally grinding is avoided if possible.

<u>Examples 2 to 6</u>

Doped yttrium oxysulphide phosphors were prepared by the procedure of Example 1. In Example 3, the oxide was of Norwegian origin and supplied by Berkshire Ores Ltd as their "phosphor grade". In Example 4, the oxide was supplied by The Propane Company, as their "phosphor grade". In Examples 2, 5 and 6, the oxides were from different suppliers.

The oxide used in Example 6 had a low lanthanide ~~level, as shown in the final product analysis, and the~~ resulting product, following the method of Example 1, did not exhibit anti-Stokes properties. Thus, Example 6 is a comparative example.

The rare earth compositions were determined by using an inductively-coupled plasma atomic emission spectrometer and an inductively-coupled plasma mass spectrometer. The results are tabulated below:

Element	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Y	58.9%	61.1%	61.2%	59.9%	77.6%
Er	4.73%	4.87%	4.83%	4.85%	4.3 ppm
Yb	12.8%	11.0%	10.9%	10.8%	10.8 ppm
Ho	17.3 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Tm	7.5 ppm	<1 ppm	<1 ppm	4.7 ppm	<1 ppm
Lu	8.2 ppm	3.1 ppm	2.5 ppm	4.8 ppm	<1 ppm

In each case, the La, Gd, Tb and Dy content was each less than 1 ppm, the Nd, Sa and Eu content was each less than 2 ppm, and the Ce and Pr content each less than 3 ppm. The sulphur content (11.75%) for Example 2 was determined separately, and the oxygen content (11.82%) by subtraction.

Examples 2 and 3 were investigated by incorporation in an alkyd, modified drying oil vehicle and coating at 36 μm thickness. Using an infrared spectrofluorimeter, results indicated that maximum visible emission of the inks occurs upon excitation with radiation at a wavelength between 965-975 nm, for both samples: the visible emission wavelengths at 965-975 nm excitation were determined:

Example 2: 2 emission bands; 560 nm & 680 nm

Example 3: 2 emission bands; 565 nm & 680 nm

Inks containing 30% by weight of each phosphor in the same vehicle were coated onto plain banknote paper and subjected to a range of resistance tests. Results are tabulated below.

Test	Example 2	3	4	5
Light fastness to simulated daylight (425 $J/cm^2/h$ at 65% reactive humidity for 200 h)	5	5	5	5
~~Dry heat (100°C/2h)~~	5 Y	5 Y	5 Y	5 Y
Humidity 100% RH 38-40°C/24 h	5	5	5	5
Hot water (70°C)	-	5	5	5
Sea water	5	5	5	5
Acetone	5	5	5	5
Ethyl Acetate	5	5	5	5
Industrial Methylated Spirits	5	5	5	5
Bleach	5	5	5	5
Diethyl ether	5	5	5	5
Tetrachloroethylene	5	5	5	5
Dilute acid	5 S	5 S	5 S	5 S
Dilute alkali	5 S	5 S	5 S	5 S
Xylene	-	5	5	5

Numerial ratings are based on anti-Stokes luminescence, where

5 = No loss of luminescence property

0 = Complete loss of luminescence property

- = Not tested

Usually, there was no residual colourant; if there was, Y indicates yellow, and S slight yellowing.

Two semi-quantitative methods have been used for assessing the brightness of the phosphors. In both methods, a tungsten filament "short-wave" infra-red lamp, with filters to remove most of the visible light, has been used. In one method, two samples are adjusted to such

distances from the source that they appear of equal brightness. These relative distances represent an inverse function of the phosphor brightness, and this relationship can be determined by measuring the IR intensities at these levels. The other method is to place two samples along side each other and equidistant from the source, and then view the brighter sample through a range of neutral density filters, choosing the one which makes the samples appear of equal brightness. The first method has proved more suitable for small brightness differences (0 to 30%); the second allows quite large differences to be evaluated.

Using a combination of these two methods, the emission intensities of the various samples mentioned above have been estimated as a percentage of the brightness of the product of Example 2. Repetition of the measurements has established an accuracy of ±5%. The results are (relative brightness given in brackets):
Example 2 (100%), Example 3 (90%), Example 4 (75%),
Example 5 (>100%) Example 6 (0%).

Example 7

An intaglio ink formulation as below was prepared using the anti-Stokes product of Example 1. Dispersion was achieved by milling on a triple-roll mill. The ink was then applied to a banknote base paper which already had been printed with security indicia. The presence of the anti-Stokes material was not visually noticeable. On illumination of the document with an infrared-emitting diode, one intaglio printing was found to luminesce in the visible, giving a blue/green colour. This composition also exhibited yellow/green fluorescence (because of the presence of photoluminescing zinc sulphide) when exposed to ultra-violet light.

	Weight %
Anti-Stokes Material of Ex. 1	20.0
Zinc Sulphide Phosphor	10.0
Calcium Carbonate	29.0
Wax	2.0

Drier lead/cobalt	1.0
Aliphatic hydrocarbon solvent	13.8
Phenolic modified resin	11.0
Drying oil/alkyd resin	13.2

Example 8

A blue intaglio ink was prepared as in Example 7, except that the zinc sulphide phosphor was replaced by Fluorescent Blue UV70 (Flare Brand: Series 840). The colour of the printed ink on infrared stimulation was blue/green. It exhibited blue fluorescence under UV excitation.

Example 9

A yellow intaglio ink was prepared as in Example 7, except that the zinc sulphide phosphor was replaced by yellow pigment. When prepared and printed by intaglio, the ink was bright yellow in colour.

Upon exposure to long-wave ultraviolet radiation, the print showed no visible fluorescence. Upon exposure to infrared radiation of a wavelength between 830 and 950 nm, it exhibited a visible blue/green colour.

Intaglio-printed materials of the invention showed superior resistance to fading by natural and artificial daylight, dry heat, alkali and various aromatic and aliphatic hydrocarbon solvents, without the loss of the upwards photoconversion effects.

Example 10

A letterpress ink was prepared using the following components:

	Weight %
Anti-Stokes Material of Ex. 1	20.0
Zinc sulphide phosphor	10.0
Silica	5.0
Wax	2.0
Lead and cobalt drier	1.2
Alkyd resin, urethane and polyamide resin mixture	58.9
Aliphatic hydrocarbon solvent	2.9

When printed by letterpress at 2-5 μm thickness, the image was pale yellow/green in colour.

Upon exposure to long-wave ultraviolet radiation (e.g. 365 nm), the print showed a visible yellow/green fluorescence followed by a short period of after-glow. Upon exposure to infrared radiation of a wavelength between 830-950 nm, the print exhibited a visible colour emission dependent upon the type of material that had been incorporated into the ink vehicle.

Examples 11 and 12

Letterpress inks were prepared as in Example 10, except that the zinc sulphide phosphor was replaced by Fluorescent Blue UV70 (Flare Brand Series 840) and yellow pigment, respectively.

The inks exhibited anti-Stokes properties on infrared illumination.

Example 13

A screen-printable ink was prepared from the following components:

	Weight %
Ethyl hydroxyethylcellulose	5.0
Copal ester synthetic resin	11.0
White spirit	33.0
Butyl cellosolve solvent	3.0
Aromatic hydrocarbon solvent	8.0
Anti-Stokes Material of Ex. 1	20.0
Fluorescent Blue UV70 (Flare Brand Series 840)	10.0
Calcium carbonate	10.0

The method of preparing the ink is to:

(a) Dissolve synthetic resin copal ester in white spirit by continuous stirring.

(b) Dissolve the ethyl hydroxyethylcellulose in the miature of butyl cellosolve solvent and the aromatic hydrocarbon solvent, again by continuous stirring.

(c) Combine solutions (a) and (b).

(d) Stir the calcium carbonate, fluorescent blue compound and UPL material into the combination of step (c).

(e) Disperse the mixture using a triple roll mill to the required degree of dispersion for screen-printing inks. The material is then ready for use.

When printed at the desired wet film thickness, and allowed to dry, the resultant print appeared almost colourless but, when exposed to long-wave ultraviolet radiation, showed a bright blue fluorescence.

When exposed to infrared radiation of a wavelength between 830 and 950 nm, the print exhibited, e.g. a visible blue/green colour.

Example 14

An ink was prepared as in Example 13, except that the fluorescent blue material was replaced by zinc sulphide phosphor.

The composition emitted visible light on UV stimulation. On infrared illumination, the ink emitted visible light.

Example 15

An ink was prepared as in Example 13, except that the fluorescent blue material was replaced by yellow pigment.

CLAIMS

1. An anti-Stokes luminescent material comprising doped yttrium oxysulphide, in which the dopants comprise, by weight of the oxysulphide, 4 to 50% of Er and/or Yb, and 1 to 50 ppm of one or more other lanthanide elements.

2. A material according to claim 1, which comprises 2 to 10% Er and 5 to 15% Yb.

3. A material according to either preceding claim, in which the other lanthanide elements are selected from Lu, Tm and Ho.

4. A material according to claim 3, which comprises Lu.

5. A material according to claim 3, which comprises Lu and Tm.

6. A material according to any preceding claim, which comprises 2 to 20 ppm of the one or more other lanthanide elements.

7. A material according to any preceding claim, in the form of particles whose average size is no more than 20 μm.

8. A material according to claim 7, in which the average size of the particles is less than 10 μm.

9. A material according to claim 1, substantially as described in any of Examples 1 to 5.

10. An ink comprising a material according to any preceding claim, a vehicle and, optionally, a colourant.

11. An ink according to claim 10, substantially as described in any of Examples 7 to 15.

12. An item such as a security document, bearing a material according to any of claims 1 to 9.

13. A method for authenticating an item according to claim 12, which comprises irradiating the item with infrared light, and observing the visible light thus emitted.

Pat nts Act 1977
E amin r's r port to th Comptroll r under ection 17 (The Search Report)

Application number

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Relevant T chnical fields

(i) UK Cl (Edition K) C4S

(ii) Int Cl (Edition 5) C09K, B41M

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Search Examiner

MS N R CURTIS

Date of Search

16 MARCH 1992

Documents considered relevant following a search in respect of claims 1-13

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1248299 (GENERAL ELECTRIC COMPANY) see page 2, lines 25-41	9

Category	Identity of document and relevant passages	Rele .t to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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